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High Temperature Superconductors $REBa_2Cu_3O_7$ (RE=Y, Gd and Eu) For Possible Thermo-electric Applications

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Abstract

In this communication, we present some results on thermo-electric properties of various high temperature superconductors. We have performed measurements on three rare-earth based cuprate superconductors. All the superconductors were prepared using solid state reaction method. The XRD studies on the present samples indicate that all the samples are in single phase. We observe that among the rare-earths studied in the present work, Gd-123 has the highest value of Z. In fact around 200K, the Z-value for $GdBa_2Cu_3O_{7-\delta}$ (Gd-123) samples is about two times that of the other rare-earths like $YBa_2Cu_3O_{7-\delta}$ and $EuBa_2Cu_3O_{7-\delta}$. However with Pr-doping at the rare-earth site, we get a different trend viz. the figure of merit for $Eu_{0.95}Pr_{0.05}Ba_2Cu_3O_7$ (Eu-Pr5%) and $Gd_{0.95}Pr_{0.05}Ba_2Cu_3O_7$ (Gd-Pr5%) samples is less than their respective pristine compounds. On contrary, an almost two-fold increase is seen in $Y_{0.95}Pr_{0.05}Ba_2Cu_3O_7$(Y-Pr5%) sample compared to the pristine sample of this series.

Keywords

High Temperature Superconductors; Doping; Figure of Merit

Introduction

It is well-known that application of thermal gradient to an electric material allows the inter-conversion of two forms of energy viz. thermal and electric energy. Such materials are called thermoelectric (TE) materials and they have attracted renewed interest because of the fact that such an energy conversion systems utilize the heat wasted at high temperatures [1]. There are, in general, three types of thermo-electric effects, viz. Seebeck effect, Peltier effect and Thomson effect. Among these, Seebeck effect is of most importance. Thermoelectric energy may perhaps offer a considerable amount of electrical power from residential cogeneration and various sources of waste heat including industrial and geothermal. When coupled to an external power supply, a thermoelectric generator becomes a solid-state (Peltier) refrigerator, cooling one end and heating the other. Thus far, the widespread use of thermoelectric generators has been limited by the small efficiency of the thermoelectric materials.

The ability of a thermocouple to carry out as a thermoelectric generator is normally characterized by the thermoelectric figure of merit Z, which is related to the thermo-power S, thermal conductivity κ, and electrical conductivity σ. The thermoelectric figure of merit for a material is defined as:

$$Z= (S^2\sigma) / \kappa \qquad (°K^{-1}) \qquad (1)$$

A good TE material requires a large thermo-power, a high electrical conductivity σ, and low thermal conductivity κ. In reality it is quite difficult to get a high magnitude for Z as these three parameters do not vary independently.

Recent advances in the efficiency and understanding of thermoelectric materials has opened variety of opportunities for thermoelectric applications. Complex Zintl phases are ideal candidates for thermoelectric materials essentially due to the necessary "electron-crystal, phonon-glass" properties. Zn_4Sb_3 has a high thermoelectric figure of merit by combining a high mobility semiconductor with extremely low thermal

conductivity which can be attributed to the presence of disordered interstitial zinc atoms and nanometer sized domains [2, 3].

High temperature superconductors exhibit low electrical resistivity which suggests that these may be potential candidates as TE materials. However in superconductors, it so happens that in the superconductor state when σ is practicable infinite and S goes to zero. When material is in the normal state, σ parameter takes on lower values and S grows. The κ goes like σ: higher values in the superconducting state and lower values in the normal states. Under these circumstances it must be necessary to optimize the combination of these three parameters in order to have high thermoelectric figure of merit parameter.

Among these high temperature superconductors developed in last two decades, there are some reports on thermoelectric properties of these high T_C superconductors. In well prepared samples of $LaMCuO_4$, Z-values of the order of 10^{-4} per K have been observed [4]. Of course, these values are much smaller than those observed in good thermoelectric. Iguchi et al [5] have investigated the TE properties of $Bi_{2-x}Pb_xSr_{3-y}Y_yCo_2O_{9-\delta}$ and have reported that such ceramics show an increase in Z value with increase in temperature.

Pekala *et al.* [6] have reported Z value of about 2×10^{-5} per K for textured samples of $DyBa_2Cu_3O_{7-\delta}$. Gonzalez *et al.* [7] have investigated Z parameter for $EuBa_2Cu_3O_{7-\delta}$ and have demonstrated that Z strongly depends on the oxygen content ($7-\delta$). They have shown that oxygen deficient samples show higher Z-values. However it is well-know that electrical conductivity, thermal conductivity and thermo-power strongly depend on nature of dopants and dopant concentration [8-11], thus, it would be interesting to explore other oxide superconductors where one can modify the stoichiometry and use suitable doping in order to achieve a fairly large value of Z.

This motivated us to investigate such studies in rare-earth based high temperature superconductors like $REBa_2Cu_3O_{7-\delta}$ with RE=Y,Gd, Eu etc. In the present studies we have prepared oxygen rich compounds as their transitions are rather sharp and have higher values of transition temperatures. We have modified the structure by doping at the rare earth as well as at Cu-site. The present communication is an outcome of our earlier thermal measurements done on pristine and transition metal co-doped compounds of $RE_{0.95}Pr_{0.05}Ba_2Cu_3O_{7-\delta}$ with RE=Y, Gd and Eu [9-11]. The thermal conductivity and thermo- power measurements were carried out in the temperature range 10-300K in a closed cycle refrigerator using a direct pulse method.

Experimental Techniques

Oxygen rich samples in the present work were prepared using solid state reaction method [10]. The stoichiometric amount of the required constituent materials Y_2O_3 (or Gd_2O_3 or Dy_2O_3, $BaCO_3$, CuO, Pr_6O_{11}, Fe_2O_3, MnO, NiO, and ZnO) were ground well in agate mortar and calcined in air at 930°C for 12 hours. The process of calcination and grinding was repeated three times in order to ensure the homogeneity of the sample stoichiometry. The calcined powder was pressed into bars of dimensions using a hydraulic press. The samples were then annealed in flowing oxygen at 950°C for 36hr and finally slow cooled to room temperature. Oxygen content of each sample was determined using standard iodometric titration.

Temperature dependent electrical resistivity was measured using four probe method. Thermo-power and thermal conductivity measurements were performed simultaneously using direct pulse method. The experimental details of electrical and thermal measurements are described in our previous communications [9-11].

Results and Discussion

Room temperature XRD were performed to determine the quality of the samples and to estimate the lattice parameters of the samples used in the present investigation. Figure 1 shows the XRD patterns for typical samples of $Y_{0.95}Pr_{0.05}Ba_2(Cu_{1-x}M_x)_3O_{7-\delta}$ (where, M = Mn, Fe, Ni and Zn). These patterns were obtained using a Rigaku Mini-Flex II X-Ray diffractometer WITH CuKα radiation as source.

Table 1 gives the lattice parameters for these samples. It is satisfying to note that there are no secondary phases within limitations of XRD. One can see from table 1 that the lattice parameters do not change appreciably for 5%Pr doped samples. However, with co-doping we observe changes in lattice parameters. The XRD patterns of other rare-earth series are reported in our earlier communications [10,11].

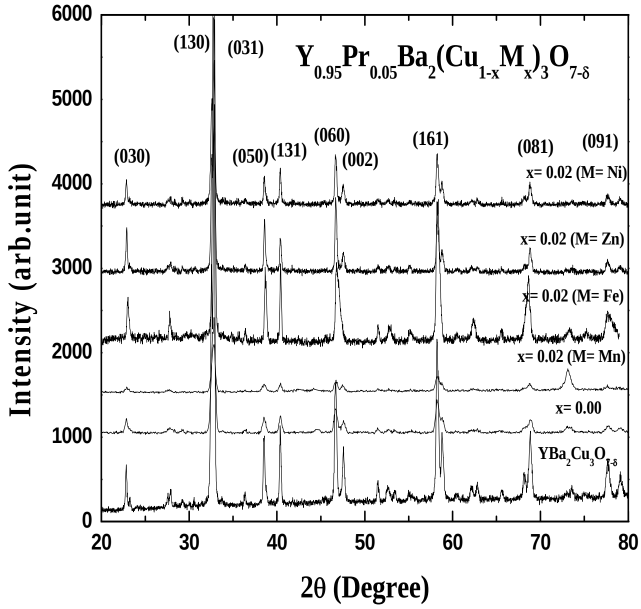

FIG 1 XRD pattern of $Y_{0.95}Pr_{0.05}Ba_2(Cu_{1-x}M_x)_3O_{7-\delta}$

Figure 2 shows the temperature dependence of figure of merit for pristine, Pr-doped as well as co-doped samples of $Y_{0.95}Pr_{0.05}Ba_2(Cu_{1-x}M_x)_3O_{7-\delta}$ and it is seen that Z value for pristine sample of $YBa_2Cu_3O_{7-\delta}$ (Y-123) remains almost constant for the temperature range 90<T<200 K. It may be mentioned that one can not estimate Z values below 90K because in this range of temperatures, σ tends to infinity and S tends to zero. However, for the Pr doped compound $Y_{0.95}Pr_{0.05}Ba_2Cu_3O_{7-\delta}$ (Y-Pr5%), the trend in the temperature range of 140<T<200K is identical to that of the pristine sample i.e. *Z* value almost remains constant. We have limited the concentration of Pr-doping to 5% and the co-doping is limited to 2% in order to reduce disordering effect of impurity, rather the electronic effects dominate over the latter. Low doping also does not alter the structure of the compounds which can be seen from table 1.

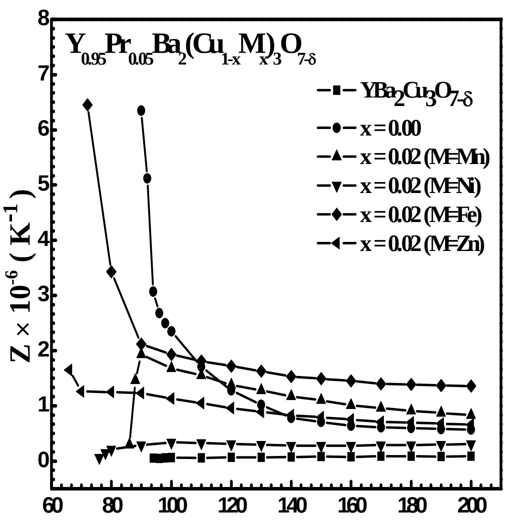

FIG 2 VARIATION OF FIGURE OF MERIT WITH TEMPERATURE OF $Y_{0.95}Pr_{0.05}Ba_2Cu_{2.94}M_{0.06}O_{7-\delta}$ SAMPLES FOR VARIOUS M

TABLE 1 Lattice parameters for $Y_{0.95}Pr_{0.05}Ba_2(Cu_{1-x}M_x)_3O_{7-\delta}$ (where, M = Mn, Fe, Ni and Zn)

Sample	*a* [Å]	*b* [Å]	*c* [Å]
$YBa_2Cu_3O_{7-\delta}$	3.819	3.888	11.666
$Y_{0.95}Pr_{0.05}Ba_2Cu_3O_{7-\delta}$	3.816	3.884	11.667
$Y_{0.95}Pr_{0.05}Ba_2Cu_{2.94}Mn_{0.06}O_{7-\delta}$	3.825	3.884	11.679
$Y_{0.95}Pr_{0.05}Ba_2Cu_{2.94}Fe_{0.06}O_{7-\delta}$	3.858	3.889	11.704
$Y_{0.95}Pr_{0.05}Ba_2Cu_{2.94}Ni_{0.06}O_{7-\delta}$	3.823	3.898	11.661
$Y_{0.95}Pr_{0.05}Ba_2Cu_{2.94}Zn_{0.06}O_{7-\delta}$	3.818	3.872	11.656

However, in the temperature range of 77-90K, we observe that Z decreases with increase in temperature. In fact at around 80K, Z attains a value about five times that in the constant region. With co- doping at copper site, Z increases for dopants such as Fe, Zn and Mn. However for Ni doping, Z decreases and lies almost between the curves of Y-123 and Y-Pr5% samples. For pure sample of Y-123, Rodríguez *et al.* [12] have reported Z value of about 1×10^{-7} per K (at 100 K) whereas, the value obtained at 100 K in the present studies is of about 0.6×10^{-7} per K. Thus the Z value of pristine sample used in present studies matches well with that reported by Rodríguez *et al*. [12].

Figure 3 shows the temperature dependence of Z for various samples of $Gd_{0.95}Pr_{0.05}Ba_2(Cu_{1-x}M_x)_3O_{7-\delta}$ (where, M = Mn, Fe, Ni and Zn). It is seen that pristine sample of Gd-123, exhibits the highest value of *Z* compared with the co-doped samples. However with Pr doping, a decrease in *Z* is observed. For dopants such as Mn and Fe, we have obtained higher values of *Z*, on contrary, for dopants such as Ni and Zn a decrease in *Z* is observed. To the best of our knowledge, there are no reports on figure of merit for Gd-based system. Now, we compare these results with that of Y-123 system. We can see that the two rare-erath based systems behave in different way. Pristine Y-123 compound exhibits lowest value of Z and with doping we observe an increase in Z values. On the other hand, in Gd-123 system, the pristine compound shows largest value and for all doped samples the Z values are smaller than that of pristine sample.

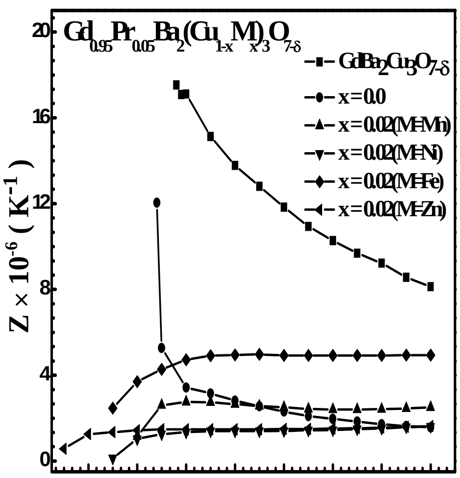

FIG 3 VARIATION OF FIGURE OF MERIT WITH TEMPERATURE OF $Gd_{0.95}Pr_{0.05}Ba_2Cu_{2.94}M_{0.06}O_{7-\delta}$ SAMPLES FOR VARIOUS M

Figure 4 depicts the temperature variation of Z for pristine and co-doped samples of $Eu_{0.95}Pr_{0.05}Ba_2(Cu_{1-x}M_x)_3O_{7-\delta}$ (where, M = Mn, Fe, Ni and Zn). This system behaves similar to the Gd-based samples. One can observe that the pure sample of $EuBa_2Cu_3O_{7-\delta}$ exhibits maximum value of Z. It is observed that with 5% Pr doping, Z decreases and with co-doping by transition metals, there is further decrease in Z value.

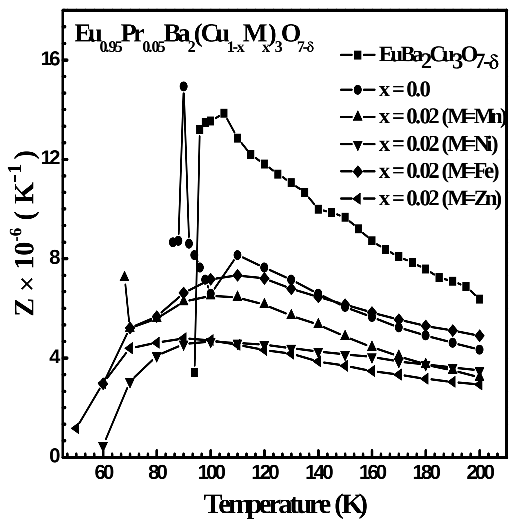

FIG. 4 VARIATION OF FIGURE OF MERIT WITH TEMPERATURE OF $Eu_{0.95}Pr_{0.05}Ba_2Cu_{2.94}M_{0.06}O_{7-\delta}$ SAMPLES FOR VARIOUS M

To the best of our knowledge there is only one report on figure of merit of $EuBa_2Cu_3O_{7-\delta}$ samples. For pure sample of $EuBa_2Cu_3O_{7-\delta}$, González *et al.* [7] have reported Z value of 8.5×10^{-8} per K (at 100K) whereas the value obtained at 100 K in the present investigations is 13×10^{-6} per K. This large difference in Z values is attributed to the fact that the sample in the present investigation has lower resistivity compared to that reported by Gonzalez *et al.* [7].

We also compare Z value at 200 K. The value of Z in presently investigated sample is 6.4×10^{-6} per K, whereas González *et al.* [7] have obtained 4.6×10^{-8} per K. We thus observe that purity of samples is an important criterion in choosing a superconductor for thermo-electric device. It would be interesting to change the oxygen content and see the effect of oxygen content on the figure of merit. It would also be of interest to change the structure of the doped superconductors by increasing the doping content.

We now compare the figure of merit for the pristine compounds of different rare-earths which show remarkable difference in behavior. This is depicted in figure 5. One can see that Gd-based superconductors show the maximum ZT-value at all the temperatures. We have plotted a dimensionless quantity ZT instead of Z for comparison.

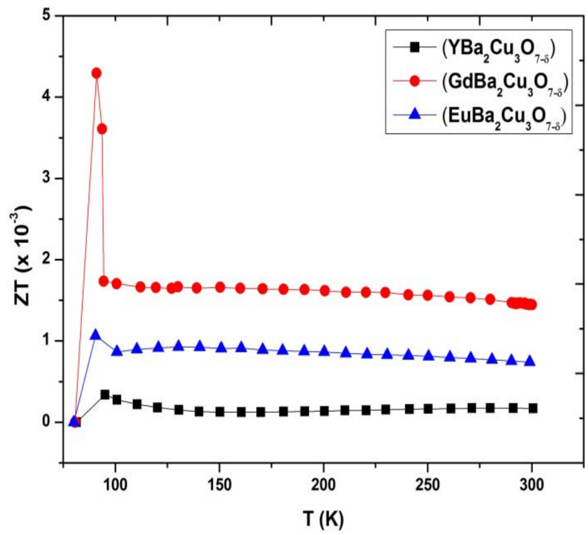

FIG. 5 VARIATION OF ZT FOR VARIOUS RE-BASED PRISTINE SAMPLES

Conclusions

In the present work we have investigated the effect of doping on the thermo-electric properties of some pristine and doped samples of high temperature superconductors. We observe that the thermo-electric figure of merit depends on the type of rare-earth used.

It is seen that among the rare-earths studied in the present work, Gd-based superconductor shows almost two fold Z values compared to other rare-earths. Y-based superconductor has the least ZT-value.

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Geetha, Manjunatha S.O. and Benedict Christopher J. are Research Scholars working under the supervision of the first author.